Thermally-induced chemistry and the Jovian icy satellites: A laboratory study of the formation of sulfur oxyanions

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[1] Laboratory experiments have demonstrated that magnetospheric radiation in the Jovian system drives reaction chemistry in ices at temperatures relevant to Europa and other icy satellites. Here we present new results on thermally-induced reactions at 50--100 K in solid H₂O-SO₂ mixtures, reactions that take place without the need for a high-radiation environment. We find that H₂O and SO₂ react to produce sulfur oxyanions, such as bisulfite, that as much as 30% of the SO₂ can be consumed through this reaction, and that the products remain in the ice when the temperature is lowered, indicating that these reactions are irreversible. Our results suggest that thermally-induced reactions can alter the chemistry at temperatures relevant to the icy satellites in the Jovian system. Citation: Loeffler, M. J., and R. L. Hudson (2010), Thermally-induced chemistry and the Jovian icy satellites: A laboratory study of the formation of sulfur oxyanions, Geophys. Res. Lett., 37, L19201, doi:10.1029/2010GL044553.

1. Introduction

[2] Numerous laboratory studies by our group and others [e.g., Moore and Hudson, 2000; Gonis et al., 2004; Loeffler et al., 2006] have demonstrated that magnetospheric radiation in the Jovian system can drive chemical and physical changes in the surface ice of satellites such as Europa. In contrast, it does not appear to be widely recognized that thermally-induced reactions also can occur in ices at temperatures on the order of 80 K even if radiation is not present. Here we report recent experiments on one such set of reactions, namely those involving H₂O and SO₂, two molecules that are believed to be present on Europa, Ganymede, and Callisto [Lane et al., 1981; McCord et al., 1998a].

[3] Remote sensing of the Jovian satellites has revealed and helped to identify surface materials including H₂O ice [Kieffer, 1957; Johnson and McCord, 1971], SO₂ [Lane et al., 1981], CO₂ [Hansen and McCord, 2008], H₂O₂ [Carlson et al., 1999a], O₂ [Calvin et al., 1996], O₃ [Noll et al., 1999b], and hydrated materials [Carlson et al., 1999b; McCord et al., 1998b]. Formation of some of these species is readily explained by low-temperature radiolysis of ices. For example, it has been shown that the H₂O₂ abundance derived from Galileo-NIMS data is consistent with what is expected from a consideration of the Jovian radiation environment and laboratory work on the radiolysis chemistry of H₂O [Carlson et al., 1999a]. More-recent experiments by Moore et al. [2007] with H₂O + SO₂ ices demonstrated that their radiolysis at 86 -- 132 K produces hydronium (H₃O⁺) and sulfate (SO₄²⁻) ions that, after warming under vacuum to remove water, yield H₂SO₄·H₂O. Similar experiments with H₂O + H₂S ices led to H₂SO₄ · 4 H₂O. The low-temperature observation of H₃O⁺ and SO₄²⁻, as opposed to H₂SO₄, was in keeping with the strongly-acidic nature of the latter and the high abundance of H₂O molecules in the ice.

[4] Although the low temperatures of the icy Jovian satellites give little hope for purely thermal chemistry, thermodynamic equilibrium constants (denoted K) nevertheless are suggestive. The acid-base reaction between H₂O and CO₂, two molecules widely observed in solar system ices, is

\[
2 \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^- \quad (1)
\]

with \( K \approx 10^{-7} \) near room temperature [Soli and Byrne, 2002]. While this value cannot be uncritically applied to cryogenic temperatures, it does suggest that purely-thermal formation of HSO₄⁻ is unlikely at ~100 K in H₂O-ice. In agreement with this, none of the earlier papers on H₂O + CO₂ ices [e.g., Sandford and Allamandola, 1990; Hudson and Donn, 1991] reported ion formation. This low equilibrium constant contrasts strongly with the high degree of ionization for the strong acid H₂SO₄ in water, with \( K \approx 10^2 \) for

\[
\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^- \quad (2)
\]

and a substantial subsequent dissociation of HSO₄⁻ into SO₄²⁻ [Williams and Flate, da Silva, 2000; Lund Myhre et al., 2003]. Correspondingly, our recent ice experiments, described above, showed H₂O⁺, HSO₄⁻, and SO₄²⁻, but no detectable H₂SO₄ until the water was removed [Moore et al., 2007].

[5] We now consider a case intermediate between H₂O + CO₂ and H₂O + H₂SO₄ ices, namely solid-phase mixtures of H₂O and SO₂. Sulfur dioxide in aqueous solution reacts according to

\[
2 \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{O}_2^+ + \text{HOSO}_3^- (\text{and/or HSO}_3^-) \quad (3)
\]

with \( K \approx 10^{-2} \) [Scott and Hobbs, 1967], which suggests that this reaction might be observed in ices. Therefore, in the experiments described here we have used infrared (IR) spectroscopy to study solid H₂O + SO₂ mixtures at temperatures that are relevant to the icy Jovian satellites. We
already described. Adding CO$_2$ and CH$_4$ (3-20%) to our H$_2$O + SO$_2$ ices failed to block the growth of the IR features in the 1100 - 950 cm$^{-1}$ region of Figure 1. Finally, a few D$_2$O + SO$_2$ ices were studied. The IR features shown growing with temperature in Figure 1 were essentially unchanged by the presence of deuterium.

4. Discussion

[14] Figure 1, and the supporting experiments already described, showed that thermal chemistry took place in our H$_2$O + SO$_2$ ices. From reaction (3) we expect the formation of bisulfite on warming a H$_2$O + SO$_2$ mixture, but from there the reaction chemistry becomes complex. Ab initio calculations of Pooge et al. (2004) suggest that the initially-formed species in solution should be HOSO$_2^-$, which on further reaction isomerizes to HSO$_3^-$. Strong support for the latter comes from our observation of a band near 2543 cm$^{-1}$ (3.93 μm) that grows in with temperature. A similar band has been assigned to the SH stretch in HSO$_3^-$ by others (Connick et al., 1982; Hisatsune and Heicklen, 1975). The two features in the 1100 - 1000 cm$^{-1}$ region of Figure 1 resemble the bisulfite bands shown in papers of Erman and Ewing (2002, Figure 3), and Pichler et al. (1997, Figure 1).

[15] All of these earlier papers support an assignment of the 1034 and 1013 cm$^{-1}$ features of Figure 1 to the S-O stretching vibrations of the two forms of the bisulfite anion, HOSO$_2^-$ and HSO$_3^-$, although it is difficult to say which band corresponds to which anion. Assigning these features to S-O stretching vibrations is also consistent with the D$_2$O + SO$_2$ ices we studied, since these same bands were unaffected by the presence of deuterium. An alternative assignment, proposed by Zhang and Ewing (2002), suggests that our 1034 feature may be a superposition of absorptions from both anions, while the 1013 cm$^{-1}$ band may be from a bisulfite dimer. The 958-cm$^{-1}$ feature in Figure 1 agrees with the position of the most intense band of pyrosulfite (S$_2$O$_3^{2-}$, also called metabisulfite and disulfite in the literature). This anion also has a weaker, broader band near 1152 cm$^{-1}$, which we also observed (see Erman and Ewing, 2005). We note that our 958-cm$^{-1}$ feature is not due to SO$_3^2-$, which we observed at 927 cm$^{-1}$ on warming ices made of H$_2$O + SO$_2$ + NH$_3$ (Hisatsune and Heicklen, 1975).

[16] To summarize, our observations and spectral assignments are consistent with thermal chemistry that converts SO$_2$ in H$_2$O + SO$_2$ ices into sulfur oxyanions. Although the precise reaction sequence remains unknown, the following path seems reasonable:

\[
\text{SO}_2 \rightarrow \text{HOSO}_2^- \rightarrow \text{HSO}_3^- \rightarrow \text{S}_2\text{O}_3^{2-} \quad (4)
\]

Formation of S$_2$O$_3^{2-}$ is possible through

\[
2 \text{HSO}_3^- \rightarrow \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \quad (5)
\]

or a similar reaction with the other form of bisulfite [Zhang and Ewing, 2002], or a reaction involving both isomers. The most-likely positive counter-ion in our ices is hydronium (H$_3$O$^+$), with its IR bands obscured by overlap with those of H$_2$O itself. Comparing the upper and lower traces in Figure 1 (bottom), for before and after anion formation, we find a slight broadening to the left of the H$_2$O-ice feature at 1650 cm$^{-1}$, in the region where H$_3$O$^+$, and other forms of the hydrated proton, have an IR absorbance (Kim et al., 2002).

[17] To quantify the conversion of SO$_2$ into ions, we measured the SO$_2$ present in ice samples as a function of deposition temperature and during heating, and assumed that all SO$_2$ lost went into ion formation. Results are presented in Figure 2. The upper panel shows that the amount of SO$_2$ that reacted rose with deposition temperature such that 25 - 30% of the SO$_2$ had formed sulfur oxyanions by 100 K. Figure 2 also shows that for a H$_2$O + SO$_2$ sample made at 50 K, the fraction of SO$_2$ that reacted when the ice was warmed at 1 K/min increased with temperature. By 100 K about 18% of the SO$_2$ had been converted into ions, and the reaction continued at 100 K until the amount converted reached an equilibrium value of about 25%. Figure 2 (bottom) also shows that at the highest temperature (100 K) of these experiments, SO$_2$ sublimation from the ice was negligible, indicating that the decrease in SO$_2$ abundance below 100 K was entirely due to ion formation. The overall result of these measurements is that our H$_2$O + SO$_2$ ices showed as much as a 30% conversion of SO$_2$ into ions by the time 100 K was reached. Total ion abundances on the order of a few percent were achieved. Finally, we note that the ion abundance continued to increase as we warmed our samples to ~150 K, at which point the SO$_2$ band had decreased by 35-60%. However, we cannot discount that a minor amount of the decrease in the SO$_2$ band area could be due to sublimation, and thus this value is an upper limit for the amount of SO$_2$ converted to sulfur oxyanions for the concentrations studied here.

[18] Thermal reactions in H$_2$O + SO$_2$ ices have rarely been mentioned in the literature. In an earlier paper [Moore et al., 2007] we noted IR bands of ions in some of our spectra, without considering their origin and implications. In an older publication by Fink and Stull [1984], the mid-IR spectrum of an ice made of H$_2$O + SO$_2$ + CO$_2$ (80:19:1.2) was presented.
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